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THE CHLOROFORM EXTRACTION OF THE 4-HEPTANONE OXIME COMPLEXES OF PALLADIUM, GOLD AND SILVER.

LEON T. DUPUIS
University of Windsor

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THE CHLOROFORM EXTRACTION OF THE 4-HEPTANONE OXIME COMPLEXES OF PALLADIUM, GOLD AND SILVER

by

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A Dissertation
Submitted to the Faculty of Graduate Studies through the
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ABSTRACT

PART II

A method is outlined for the determination of trace amounts of palladium (II) in a noble-metals-bearing sulfide concentrate using the 4-heptanone oxime extraction procedure. The average result of 0.335 oz./ton agrees favourably with the recommended value of 0.37 oz./ton.

PART III

A procedure is outlined for the quantitative separation of ultra-trace amounts of palladium (II) from large volumes of hydrochloric acid solutions and hydrochloric acid solutions containing macro amounts of copper (II), nickel (II), cobalt (II) and iron (III).

PART IV

A procedure is outlined for the separation of microgram amounts of gold (III) from milligram amounts of copper (II), iron (III) or nickel (II) in hydrochloric acid solutions by the chloroform extraction of the gold (III) 4-heptanone oxime complex. The effects due to oxime concentration and multiple extractions are described.

PART V

A preliminary study of the extraction of silver (I) into chloroform after reaction with 4-heptanone oxime is made. The effects due to nitric acid concentration, nitrate ion concentration, oxime concentration and silver (I) concentration on the distribution of silver (I) between aqueous and 4-heptanone oxime-chloroform layers are described. Two models are developed to explain the extraction of silver (I) from solutions low in nitric acid concentrations and relatively high in nitric acid concentrations.

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PART I

GENERAL INTRODUCTION

A. Separation and Uses of Palladium, Gold and Silver

Separation of interferences from species to be determined is an important step in quantitative analytical procedures. The ideal quantitative method would be a specific one; that is, it would measure or separate the desired species accurately in the presence of any combination of foreign substances. Unfortunately, few analytical methods achieve specificity, although many are selective and can be used to determine or separate an ion or ions in the presence of certain foreign ions or compounds.

Although the development of instrumental methods of analysis in relatively recent years has sometimes succeeded in placing actual methods of separation in a minor position in analytical work, unfortunately it has not been possible to eliminate totally the need for separations prior to many quantitative analyses. In many cases it is still necessary to remove interfering substances and this is especially true in the analysis of the noble metals and silver.

Information dealing with solution composition of useful analytical systems (such as the effects of acidity, salt content, foreign ions, reaction times and reagent selectivity) can be of great benefit to researchers. Not only can this

information help in improving analysis procedures, but it can also be useful in the development of more economical separation and purification methods by such techniques as ion exchange, fire assay, precipitation, chromatography and solvent extraction. It is the latter method which is studied in the present work.

In view of the general usefulness of the noble metals and silver and the fact that they are produced in commercial quantities as by-products from the sulfide ores of Sudbury and South Africa in which they occur in only trace amounts, the separation of the platinum group metals and silver from large quantities of the base metals has long been a challenge to the analytical chemist.

With the cost per ounce of gold rising daily in the international market place, there can be no question as to the great economic value placed on it by the modern world. In addition to its significance as a monetary standard, this precious metal and its sister metals, palladium and silver, are in demand for a variety of other reasons. Besides being used in the fabrication of jewellery, dentures, and other personal adornments, these metals play a major role in many industrial processes.

The electrical and electronics industries, for example, require them in large quantities for use in the manufacture of corrosion-resistant wires and contacts. Palladium has great importance as a catalyst in hydrogenation and dehydrogenation reactions. Large amounts of palladium are used by the automobile industry in its catalytic converters.

The analysis of the platinum group metals and silver is complicated by the fact that very rarely does only one of them occur in the material to be analyzed. Usually before the determination of each metal a separation is imperative, and the separation step definitely represents the most difficult problem to the analyst, especially in the case of micro-amounts.

In the area of ore analysis, the problem of interferences still continues to necessitate the development of good separational methods for the noble metals and silver from naturally occurring complex matrices. The need for quick, reliable information on the commercial value of poorer grade ores has become necessarily important due to large demands and the ever-increasing cost of these metals.

With regard to the separation and determination of the noble metals, extensive reviews of the literature have been written by Beamish [1-6]. This author has also published distinguished books on the present chemistry and analysis of the noble metals [7,8].

B. Oximes as Analytical Reagents

Many complexing agents have been proposed for the extraction of palladium. The majority of these reagents are azo compounds, organic sulfur compounds or oximes.

The high selectivity of oximes for palladium has encouraged the use of these reagents for gravimetric and extractive pruposes. One of the greatest finds was dimethylglyoxime. Its application to the quantitative analysis of palladium was reported in 1912 [9,10].

Since then a great many oxime analogues have been proposed in an effort to effect some improvements on the performance of dimethylglyoxime, such as a better gravimetric factor, improved physical characteristics of the precipitate, and greater solubility of the reagent.

The use of oximes by Holland and co-workers has been applied to the determination of both gold and palladium. The reagent 2,2´-dithienyl ketoxime [11,12] was employed for the gravimetric separation and determination of these metals. As well, the use of oximes was extended to spectrophotometric methods for determining gold and palladium. Such reagents as 2,2´-dipyridyl ketoxime [13,14] and 2,2´-dipyridyl-α-glyoxime [15,16] were proposed. 2-pyridyl-2-thienyl-2-ketoxime [17] was used in the determination of microgram amounts of palladium and is currently being studied as a method for the colourimetric determination of gold [18].

Although these compounds were of use in the determination of trace amounts of palladium and gold, they were not applicable to the quantitative extraction of milligram amounts of

these metals from acid solutions, or to the quantitative separation of microgram amounts from large amounts of the other platinum metals or the associated base metals — nickel, copper and iron.

C. Related Research with Symmetrical Alkyl Ketoximes

The high selectivity of oximes for palladium encouraged an investigation in this laboratory of the reaction between symmetrical alkyl ketoximes and palladium. The results of a preliminary study by DiMenna [19] indicated that relatively large amounts of palladium (II) chloride could be extracted into chloroform after reaction with alkyl ketoximes (2-propanone oxime, 3-pentanone oxime, 4-heptanone oxime and 5-nonanone oxime) in aqueous alcohol solutions.

The elemental and infra red analysis of the isolated complexes indicated that the following reaction took place:

$$2\,(R\text{-}\underset{\underset{N\text{-}OH}{\|}}{C}\text{-}R) + PdCl_2 \longrightarrow (R\text{-}\underset{\underset{N\text{-}OH}{\|}}{C}\text{-}R)_2 \cdot PdCl_2$$

Research by Dunn was further projected to explain the reaction course of the above equation as well as to give a better understanding of the products formed.

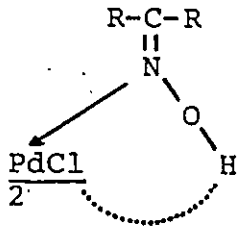
A comparative study [20] of the chloroform extraction of the 4-heptanone oxime and 2,4-dimethyl-3-pentanone oxime complexes of palladium (II) chloride demonstrated that conditions of chloride ion concentration, oxime concentration, oxime hydrolysis in acid solution and sterric effects all took part in the extraction of palladium (II) chloride. The results of this study indicated the following reaction course:

$$PdCl_4^{=} \longrightarrow PdCl_3^{-} + Cl^{-}$$

$$PdCl_3^{-} \longrightarrow PdCl_2 + Cl^{-}$$

$$PdCl_2 + 2R\text{-}\underset{\underset{N\text{-}OH}{\|}}{C}\text{-}R \longrightarrow (R\text{-}\underset{\underset{N\text{-}OH}{\|}}{C}\text{-}R)_2 \cdot PdCl_2$$

To better appreciate the products formed, a study of the infra red spectra of the free and complexed ligands was made [21]. From this data, Dunn assigned the following structure for the palladium (II) chloride alkyl oxime complex:



Further studies have been made on the effect of hydrochloric [22] nitric and sulfuric acid [23] concentrations on the efficiency of the 4-heptanone oxime solvent extraction procedures in extracting palladium (II) at the milligram level.

Subsequent research was carried out with 4-heptanone oxime by Walker into the applicability of this reagent to selectively separate palladium from the other platinum group metals and associated base metals by solvent extraction procedures [22,24-28].

During these studies it was also shown that milligram amounts of gold (III) may be extracted from 0.1M hydrochloric

acid into chloroform after reaction with 4-heptanone oxime [29].

It is from this point that the study of the applications of the analytical reagent 4-heptanone oxime has been expanded. In the present work methods have been developed for the separation of trace amounts of palladium (II) from a noble-metals-bearing sulfide concentrate and ultra trace amounts from solutions containing macro quantities of associated base metals. A procedure for the separation of microgram amounts of gold (III) from milligram amounts of the base metals copper, iron and nickel, was developed utilizing 4-heptanone oxime. A solvent extraction study of the distribution of silver (I) between aqueous and chloroform-4-heptanone oxime phases was initiated.

The details of all these investigations will be presented in this dissertation.

PART II

THE SEPARATION AND DETERMINATION OF TRACE AMOUNTS OF PALLADIUM IN A NOBLE-METALS-BEARING SULFIDE CONCENTRATE

PART II

THE SEPARATION AND DETERMINATION OF TRACE AMOUNTS OF PALLADIUM IN A NOBLE-METALS-BEARING SULFIDE CONCENTRATE

A. Introduction

The Sudbury ore deposits in Canada are a rich and important source of both base and noble metals. They contain about 3% nickel and copper as sulfides and average a platinum metal content of 0.02 oz. per ton [30].

However, the analysis of palladium in the concentrates produced by the processing of these ores is difficult. The problem is created by two factors: interferences from the large amounts of base metals they contain and the presence of associated platinum metals and of gold. Few procedures have been reported in the literature for the separation of palladium (II) from large amounts of nickel, copper and iron.

Patil and Shinde [31] extracted microgram amounts of palladium from milligram amounts of nickel, cobalt and iridium, but platinum, rhodium and iron are co-extracted by their process.

Ziegler and Pape [33] reported the separation of trace amounts of palladium from large amounts of rhodium, cobalt and nickel, but platinum, copper and iron interfere, and necessitate prior separation to obtain reasonable results.

In the investigations of the analytical reagent 4-

heptanone oxime by Holland and co-workers, gram amounts of copper, nickel and iron did not interfere in the extraction of microgram amounts of palladium [27]. Studies with the platinum metals revealed that platinum (IV) and rhodium (III) did not interfere and only minor amounts of iridium (IV) at the milligram level were co-extracted [25]. These investigations have been utilized in the development of procedures for the separation and determination of palladium in the presence of milligram amounts of platinum and microgram amounts of rhodium and iridium [26]. This procedure was found suitable for the analysis of synthetic ore and matte samples containing gram amounts of nickel and copper and milligram amounts of iron [28].

The purpose of the present work was to investigate this type of solvent extraction procedure using 4-heptanone oxime for the separation and determination of palladium in a noble-metals-bearing sulfide concentrate containing relatively large amounts of iron and requiring a hydrofluoric acid treatment for complete solution of the sample.

B. Experimental

1. Apparatus and Materials

a) Instruments

Spectrophotometric measurements were made with a Beckman DB spectrophotometer, using 1.00 cm. matched silica cells. A Sargent Model Ls pH meter was used for all pH measurements. Separatory funnels fitted with teflon stopcocks were used throughout.

b) 4-Heptanone Oxime

The oxime was prepared by refluxing 4-heptanone with hydroxylamine hydrochloride in an alkaline alcohol-water mixture, evaporating the excess alcohol, extracting the oily oxime with diethyl ether, rotoevaporating the excess ether and distilling under vacuum.

c) Palladium Chloride

Purified, anhydrous palladium chloride was obtained from the Fisher Scientific Company.

d) Standard Palladium (II) Chloride Solution

A stock solution was prepared by dissolving anhydrous palladium (II) chloride in 25 ml. of hot concentrated hydrochloric acid to yield a clear reddish-brown syrup. The syrup was diluted to 1 litre with distilled deionized water after filtering through a sintered glass crucible. The solution was standardized gravimetrically with 2,2'-dipyridyl ketoxime [33]. An appropriate diluted stock solution was made from the above standardized stock solution, to contain approximately 22 µg. per ml.

e) Noble-Metals-Bearing Sulfide Concentrate PTC Canadian Certified Reference Material Project Mines Branch [34] (% Ni, 9.42; % Cu, 5.16; % S, 23.5; % Fe 26.9; recommended Pd content, 0.37 oz./ton).

f) Miscellaneous Reagents

The chloroform, hydrochloric acid, hydrofluoric acid, nitric acid, sulfuric acid, and sodium chlorate were all A.C.S. grade. All other chemicals were of reagent grade.

g) Water

Distilled deionized water was used throughout.

2. Procedures

a) Separation of Palladium from the Standard Reference Sulfide Concentrate

Before the sulfide concentrate could be analyzed, it first had to be dissolved, this was accomplished by an acid leaching process.

Weigh accurately, approximately 7 grams of the standard sulfide concentrate into a 1 litre beaker. To the beaker add 100 ml. of concentrated hydrochloric acid and heat the resulting mixture gently with stirring until hydrogen sulfide ceases to evolve. Cool the solution and add slowly with stirring 30 ml. of concentrated nitric acid. Boil the mixture with evaporation to a volume of approximately 75 ml. Repeat the nitric acid treatment with evaporation three times. Cool and add 3 ml. of A.C.S. bromine carefully to dissolve the yellow sulfur that has precipitated on the surface of the solution. Heat gently until the excess bromine is expelled.

After dilution to 200 ml. with distilled water, add 30 ml. of concentrated sulfuric acid and evaporate the solution on a hot plate to dense white fumes. To the beaker add 100 ml. of distilled water and 20 ml. of concentrated nitric acid and again evaporate to fumes of sulfuric acid. Repeat the nitric acid-water treatment two times.

Dilute the solution to 200 ml. with distilled water and transfer to a covered 400 ml. teflon beaker. After evaporation to a volume of approximately 200 ml. on a sand-bath, add 20 ml. of hydrofluoric acid to dissolve the siliceous material present. Continue the evaporation until dense white fumes of sulfuric acid are evolved. Cool the beaker, add 100 ml. of distilled water and again evaporate the solution to fumes.

After dilution with distilled water, transfer the contents of the teflon beaker to a 600 ml. beaker and add a solution of 30 gm. of sodium hydroxide slowly with stirring. Adjust the apparent pH of the solution to 0.0, as indicated by a pH meter, by the alternate dropwise addition of sodium hydroxide and by hydrochloric acid solutions. Transfer the resulting clear green solution to a 500 ml. separatory funnel and dilute by the addition of 1 M hydrochloric acid to approximately 400 ml.

b) Recommended Extraction Procedure

Transfer 0.20 ml. of 4-heptanone oxime to the separatory funnel and shake for 30 seconds. Let the solution stand for 10 minutes and shake again for 30 seconds. Allow the solution to stand for another 10 minutes and extract twice with 25 ml. portions of chloroform. Transfer the chloroform extracts to

a 400 ml. beaker. Repeat the above extraction procedure with the residual aqueous layer.

c) Palladium Analysis of the Chloroform Extract

The combined chloroform extracts were evaporated to dryness on the steam bath and the residual organic matter destroyed by treatment with 0.5 gm. of sodium chlorate, 30 ml. of distilled water and 4 ml. of concentrated hydrochloric acid. Excess chlorine was expelled by repeated additions of hydrochloric acid followed by evaporation. To the solution was added distilled water and the pH adjusted to 0.0, as indicated by a pH meter, by the alternate dropwise addition of sodium hydroxide and hydrochloric acid solutions. The solution was transferred to a 250 ml. separatory funnel and diluted to 100 ml. with 1 M hydrochloric acid.

The above recommended extraction procedure was repeated, the chloroform extracts evaporated and the residual organic matter destroyed by the sodium chlorate-hydrochloric acid treatment. The palladium content was determined spectrophotometrically with 2,2'-dipyridyl ketoxime [13].

The results are summarized in Table I.

TABLE I

Separation of Palladium from a Standard Reference Concentrate

The recommended value, certified by the Canadian Mines Branch is 0.37 oz./ton

Run	Gms Concentrate Taken	Pd (II) Found oz./ton
1	7.02	0.337
2	7.00	0.364
3	7.04	0.335
4	7.00	0.329
5	7.00	0.321
6	7.00	0.335
7	7.00	0.351
8	7.01	0.343
9	7.00	0.328
10	7.01	0.328
11	7.00	0.321
12	7.01	0.333
	Average	0.335
	Standard deviation	0.012

C. Results and Discussion

The extraction procedure used for palladium (II) at the microgram level was the same as the recommended procedure for the quantitative extraction of palladium in the milligram level developed by Walker [22] except that the volume of reagent was reduced. The total volume of reagent was reduced to 0.4 ml. (2 x 0.2 m.) because of the small amounts of palladium to be recovered.

A study by Walker [27] on the effect of gram amounts of the base metals iron (III), nickel (II), and copper (II) on the palladium (II) extraction procedure had shown that small milligram amounts of these base metals are co-extracted. The interference that these metals have on subsequent spectrophotometric blanking procedures was eliminated by employing a double work-up procedure.

Also in the determinative step with 2,2´-dipyridyl ketoxime 1 ml. of 1% EDTA was added to the solutions to mask any copper (II), nickel (II) or iron (III) that might still have been present. The colourimetric method using 2,2´-dipyridyl ketoxime for the determination of palladium (II) has a standard deviation of 0.002 oz. per ton [13].

In the work-up procedure, sodium chlorate and hydrochloric acid were used to destroy the residual organic matter. To eliminate unnecessary bumping and splattering due to the precipitation of salts when evaporating to near dryness, digestion with chloric acid could have been used as an alternative method.

In initial studies it was found that after digestion with

sodium chlorate and hydrochloric acid, there often remained greasy globules and film on the sides of the beaker. Even after further digestive treatments this greasy coating persisted. The greasy material was found to be soluble in chloroform impinging upon it a faint yellow colour.

It was noted, however, that when separatory funnels containing teflon stopcocks were used the film was absent. Thus this greasy matter was attributed to stopcock grease which was carried through with the chloroform extracts. In order to avoid any blanking problems which may have occurred in subsequent colourimetric determinations, separatory funnels fitted with teflon stopcocks were used throughout the study.

The certified standard-noble-metals-bearing sulfide concentrate was obtained from the Canadian Mines Branch in Ottawa, Ontario for analysis. In order to check and compare the 4-heptanone oxime solvent extraction separation procedure a set of results were compiled for the reference concentrate. The results are shown in Table I.

The 4-heptanone oxime extraction procedure as a method for the separation of palladium gave an average value of 0.335 oz./ton on 12 results ranging from 0.32 to 0.36 oz./ton, with a standard deviation of 0.012 oz./ton.

The palladium value of 0.335 oz./ton obtained by the 4-heptanone oxime procedure agrees favourably with the recommended value of 0.37 oz./ton when one considers how the palladium content was arrived at on the reference concentrate.

The Canadian Mines Branch statistically treated 164

results obtained from a number of laboratories which in almost all cases used fire assay for the preliminary separation of the platinum metals, gold, and silver. These results ranged in value from approximately 0.2 to 0.7 oz./ton. A breakdown of these results is illustrated in Figure 1; 81.2% of the results fall within the range of 0.3 to 0.4 oz./ton while 13.9% were greater than 0.4 oz./ton and 4.9% were below 0.3 oz./ton. The statistical analysis of all of these results gave a recommended palladium content of 0.37 oz./ton for the concentrate. All the results of the present study ranging in value of 0.32 to 0.36 fall well within the 81.2% of the 164 contributed results and gave an average palladium value of 0.335 oz./ton.

A PLOT OF THE RANGE AND PERCENTAGE OF 164 RESULTS OBTAINED BY THE CANADIAN MINES BRANCH ON THE STANDARD CONCENTRATE PTC

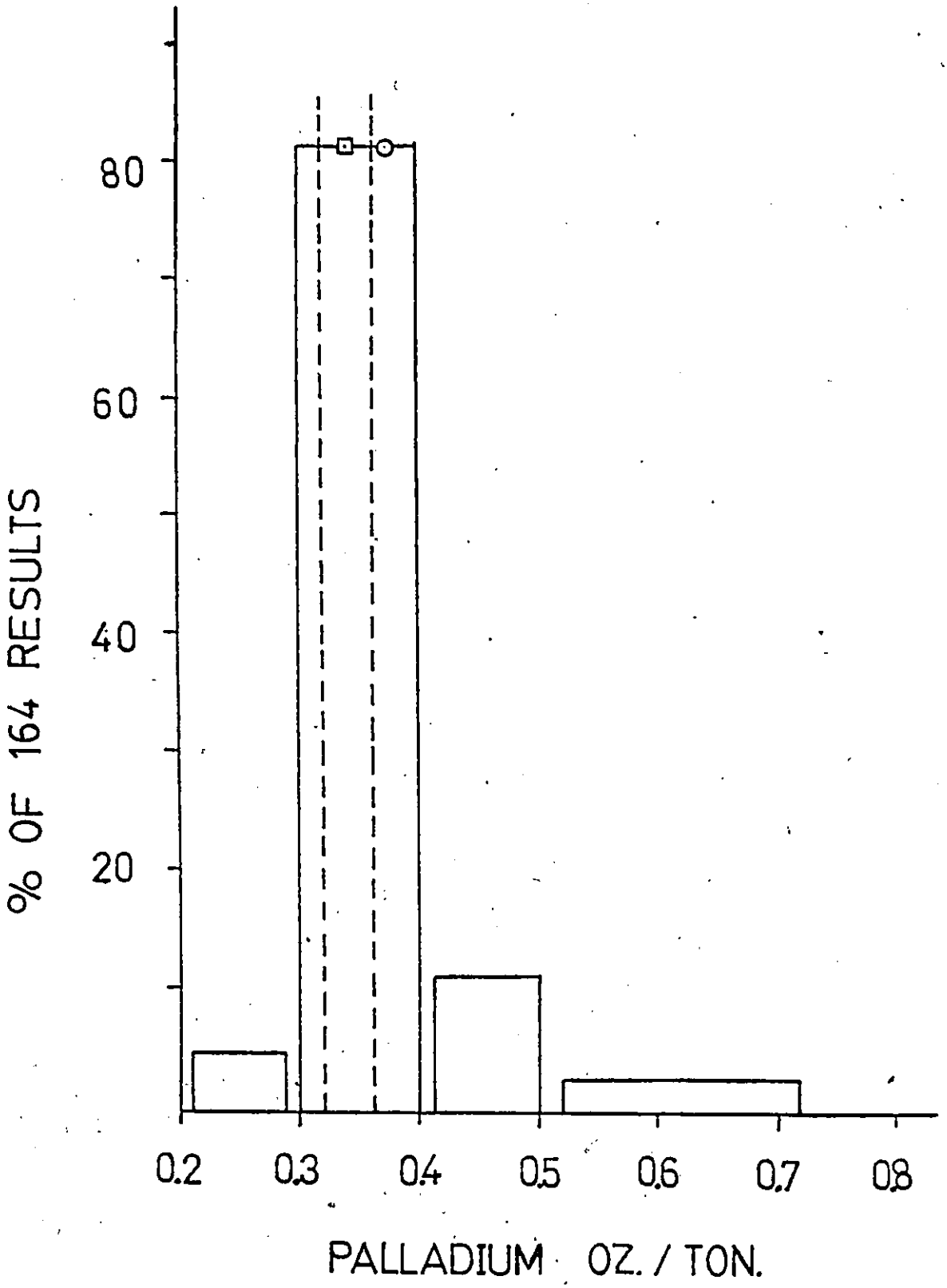
——— Range and percentage of the 164 results obtained by the Canadian mines branch.

—0— The recommended palladium content, 0.37 oz./ton

----- Range of 12 results obtained by the 4-heptanone oxime procedure.

--□-- Average palladium content obtained by the 4-heptanone oxime procedure, 0.335 oz./ton.

FIGURE 1



D. Conclusions

From the present study it can be concluded that the 4-heptanone oxime extraction procedure is capable of quantitatively separating trace amounts of palladium from a complex matrix containing large amounts of iron and requiring a hydrofluoric acid treatment for complete solution. The results are comparable to those obtained by fire assay followed by atomic absorption or spectrographic analysis.

E. Summary

The 4-heptanone oxime extraction procedure may be used for the quantitative separation of trace amounts of palladium from a noble-metals-bearing sulfide concentrate. An average palladium value of 0.335 oz./ton is obtained on the standard sulfide concentrate compared to the recommended value of 0.37 oz./ton.

A condensed version of this work has been published [35].

PART III

THE SEPARATION AND DETERMINATION OF ULTRA TRACE AMOUNTS OF PALLADIUM (II) IN SOLUTIONS CONTAINING MACRO AMOUNTS OF COPPER (II), IRON (III), COBALT (II) AND NICKEL (II)

PART III

THE SEPARATION AND DETERMINATION OF ULTRA TRACE AMOUNTS OF PALLADIUM (II) IN SOLUTIONS CONTAINING MACRO AMOUNTS OF COPPER (II), IRON (III), COBALT (II) AND NICKEL (II)

A. Introduction

A 4-heptanone oxime solvent extraction procedure has been previously outlined for the quantitative separation of microgram amounts of palladium (II) from relatively small volumes of water containing milligram amounts of nickel, copper, iron and cobalt [22, 24]. In further studies it was shown that gram quantities of nickel, copper and iron did not interfere with the recommended procedure for palladium (II) [27].

Succeeding investigations demonstrated that this procedure could be used to quantitatively separate palladium at the parts per million level from ten gram samples of a nickel-copper matte [28] and seven gram samples of a noble-metals-bearing sulfide concentrate [35].

The possibility of developing a procedure for the quantitative separation of palladium (II) at the parts per billion level then became evident from these previous studies.

The purpose of the present work constitutes the development of a procedure for the quantitative separation of palladium at the parts per billion level by the chloroform

extraction of its 4-heptanone oxime complex from relatively large volume synthetic solutions containing gram amounts of the associated base metals copper, nickel, cobalt and iron.

One aim of this procedure was that it might be applied to the determination of palladium at the parts per billion level in low grade ores. Since large weights of sample would be required, the volume of sample solutions studied were relatively large.

B. Experimental

1. Apparatus and Materials

a) Instruments

Spectrophotometric measurements were made with a Beckman Model DB spectrophotometer using 1.00 cm. matched silica cells. A Sargent Model LS pH meter was used for pH measurements, and a Corning PC-351 combination hot plate and magnetic stirrer equipped with a 2-1/2" x 3/8" stirring bar for stirring the solutions. All separatory funnels were equipped with teflon stopcocks.

b) 4-Heptanone Oxime

The 4-heptanone oxime was prepared by reaction of 4-heptanone with hydroxylamine hydrochloride as previously described [19].

c) Palladium Chloride

Purified anhydrous palladium chloride was obtained from the Fisher Scientific Company.

d) Standard Palladium (II) Chloride Solution

A stock solution was prepared by dissolving anhydrous palladium (II) chloride in 25 ml. of hot concentrated hydrochloric acid, diluting to 1 litre with distilled deionized water and standardizing gravimetrically with 2,2'-dipyridyl ketoxime [33].

e) Miscellaneous Reagents

The sodium chlorate and sodium hydroxide were A.C.S. grade. Baker analyzed hydrochloric acid was used after standardization for all concentration adjustments.

f) Base Metal Salts

The cobalt (II) chloride hexahydrate, cobalt (II) sulfate hexahydrate, copper (II) chloride dihydrate, copper (II) sulfate pentahydrate, nickel (II) chloride hexahydrate, nickel(II) sulfate hexahydrate, iron (III) chloride hexahydrate and iron (III) sulfate hydrate were all A.C.S. grade.

g) Chloroform

A.C.S. grade chloroform was used for the extraction of palladium (II) after reaction with 4-heptanone oxime and spectral grade chloroform was used for the spectrophotometric measurements of palladium (II).

h) Water

Distilled deionized water was used throughout.

2. Procedures

a) Procedure for Determining the Iron Content of the Ferric Sulfate Hydrate

The percentage of iron in the hydrated ferric sulfate was determined titrimetrically with standard potassium dichromate solution after reduction with chlorostannous acid.

b) Procedure for Preparing the Base Metal Solutions

The base metal chloride or sulfate solutions were prepared by transferring a weighed amount of the metal salt to a graduated 6000-ml. erlenmeyer flask containing 1 to 2 litres of distilled deionized water and sufficient concentrated hydrochloric acid to produce a solution that was 0.25 M in acid on dilution to the 5000-ml. mark. The solution was stirred with a magnetic stirrer until the salt dissolved.

An aliquot of palladium (II) chloride solution containing approximately 77 µg. of palladium (II) was added and the solution was diluted to the 5000-ml. mark. The final solution contained approximately 15 p.p.b. of palladium (II) and a known amount of the corresponding base metal.

c) Recommended Procedure for the Extraction of Palladium (II) from Macro Amounts of Copper, Nickel, Iron and Cobalt

Add 1 ml. of 4-heptanone oxime to the 6000 ml. erlenmeyer flask containing a known amount of a base metal dissolved in 5000 ml. of solution 0.25 M in hydrochloric acid and approximately 15 p.p.b. of palladium (II). Stir the solution vigorously for 30 minutes; add 100 ml. of chloroform, and stir rapidly for another 30 minutes. Turn off the stirrer and allow the aqueous and chloroform phases to separate for 30 minutes. Transfer most of the supernatant solution to a second 6000 ml. graduated erlenmeyer flask and the residual chloroform and aqueous layers to a 1 litre separatory funnel, rinsing with 0.25 M hydrochloric acid. Let stand until two distinct layers form. Draw off the chloroform layers into a suitable container and add the residual aqueous layer to the second 6000-ml. erlenmeyer flask. Repeat the above procedure twice, finally wash the aqueous solution by stirring with 100 ml. of chloroform.

d) Palladium Analysis of the Chloroform Extracts

Evaporate the combined chloroform extracts on a steam bath, add 30 ml. of water, 2.5 gm. of sodium chlorate, 4 ml. of hydrochloric acid, and bring to a boil. Continue heating with repeated additions of concentrated hydrochloric acid

until the solution is free of chlorine indicated by use of moistened potassium-iodide-starch impregnated test paper. Evaporate the solution to the point where sodium chloride crystals begin to form. Cool, add 50 ml. of water, and adjust the apparent pH to 0.0 by the alternate dropwise addition of hydrochloric acid and sodium hydroxide solutions.

Transfer the resulting solution to a 250 ml. graduated separatory funnel and dilute to the 100 ml. mark with 1 M hydrochloric acid. Add 0.2 ml. of 4-heptanone oxime and shake. Allow the solution to stand for 10 minutes and shake again. After an additional 10 minutes standing time, extract with two 25 ml. portions of chloroform. Transfer the chloroform extracts to a beaker. Repeat the above procedure with the residual water layer.

Evaporate the combined extracts to dryness on the steam bath. Destroy the residual organic matter by treatment with sodium chlorate and hydrochloric acid. Continue the evaporation with repeated additions of hydrochloric acid until chlorine ceases to evolve. Determine the palladium spectrophotometrically with 2,2'-dipyridyl ketoxime [13]. The results of this study are summarized in Table III.

e) Initial Study of the Efficiency of Recovering Palladium (II) at Different Concentration Levels from 5000 ml. of Water 0.25 M in Acid

An aliquot of standard palladium (II) chloride solution containing a known amount of palladium (II) was transferred to a 6000-ml. erlenmeyer flask. Sufficient hydrochloric acid was added so that on dilution to the 5000 ml. mark the solution would be 0.25 M in hydrochloric acid. The extraction and

determination procedures for palladium (II) outlined above were followed.

The results are summarized in Table II.

TABLE II

Determination of palladium (II) at the parts per billion level in 5000 ml. of water 0.25 M in hydrochloric acid

Palladium (II) added p.p.b.	Palladium (II) found* p.p.b.	% Palladium recovered	Standard Deviation p.p.b.
11.0	10.8	98.2	0.3
15.3	15.2	99.3	0.3
21.9	21.5	98.2	0.2

*Each result is the average of six determinations.

TABLE III

Determination of palladium (II) in 5000 ml. of water, 0.25 M in hydrochloric acid, containing gram amounts of copper, nickel, iron and cobalt as the chlorides and sulfates. Palladium taken as the chloride, 15.3 p.p.b.

Metal Salt	Equivalent amount of metal taken gm	Pd (II) found p.p.b.*	Standard Deviation p.p.b.
Copper (II) chloride dihydrate	10	15.2	0.2
Copper (II) sulfate pentahydrate	5	15.1	0.3
Nickel (II) chloride hexahydrate	20	15.1	0.2
Nickel (II) sulfate hexahydrate	20	15.1	0.2
Cobalt (II) chloride hexahydrate	22	15.1	0.2
Cobalt (II) sulfate hexahydrate	21	15.1	0.2
Iron (III) chloride hexahydrate	20	15.2	0.2
Iron (III) sulfate hydrated	21	15.2	0.2

*Each result is the average of six determinations.

C. Results and Discussion

The initial study of the recovery of palladium (II) at different concentration levels from 5 litres of water, 0.25 M in hydrochloric acid (shown in Table II) demonstrates that palladium (II) can be quantitatively recovered and determined over the range of 11 to 22 parts per billion. These results also indicate that acid concentration of 0.25 M and a reaction time of 30 minutes can be used to achieve quantitative recovery.

In previous studies on the extraction of trace amounts of palladium, the extraction process using 4-heptanone oxime was carried out from 1 M hydrochloric acid solutions after a 20-minute reaction time. At times of longer than 20 minutes it was found that under conditions of 1 M hydrochloric acid the oxime was hydrolyzed appreciably [36].

In the present investigation longer reaction times were employed (30 minutes) since larger volumes of solution were used. Thus the acid concentration was lowered to 0.25 M to lessen the extent of hydrolysis of the reagent to the ketone and hydroxylamine hydrochloride. An excess of the oxime (3 x 1 ml.) was also used to offset the problem of hydrolysis and increase the availability of the reagent to complex with the palladium(II).

From the results of the initial study shown in table II, it becomes evident that this method for the quantitative extraction of palladium (II) at the p.p.b. level is possible.

In order that this procedure for the extraction of ultra trace amounts of palladium be applicable it was necessary to

study the effects of macro quantities of the associated base metals under the same extraction conditions.

Preliminary investigations demonstrated that in each case the presence of large amounts of copper, nickel, iron and cobalt did not cause any interference in the separation and determination of palladium (II) at the parts per billion level. It was decided to extend the study to find the maximum amount of each of these base metals that the procedure could tolerate. The results of this study are given in Table III.

Table III shows the upper tolerable limits of each base metal that the outlined procedure will allow while still effecting quantitative separation at the parts per billion level. The recovery of palladium (II) was very good. In all cases an average concentration of about 15.1 p.p.b. was found with a standard deviation of 0.2 p.p.b. for palladium (II) taken initially at the 15.3 p.p.b. level.

D. Conclusions

With a few minor alterations, this procedure should be of use in the recovery and measurement of trace amounts of palladium in a variety of materials such as low grade ores, alloys, meteorites and in plating solutions.

To extend the use of this separation procedure into areas of further application, studies should be made with regards to the effect of more complicated matricies. Systems containing large amounts of all of the afore-mentioned base metals along with associated platinum group metals should be studied.

It is the author's opinion that the time required for the extraction procedure (30 minute mixing times) could be shortened without any appreciable loss in recovery by increasing the volume of oxime used. Further studies could be initiated to prove this.

E. Summary

In the present study a procedure is outlined for the separation and determination of palladium (II) at the parts per billion level in the presence of macro amounts of copper, nickel, cobalt and iron separately in relatively large volumes of water.

A condensed version of this work has been published [37].

PART IV

THE SEPARATION OF TRACE AMOUNTS OF GOLD (III) FROM MILLIGRAM AMOUNTS OF IRON (III), NICKEL (II) AND COPPER (II)

PART IV

THE SEPARATION OF TRACE AMOUNTS OF GOLD (III) FROM MILLIGRAM AMOUNTS OF IRON (III), NICKEL (II) AND COPPER (II)

A. Introduction

The wide applications of gold in such areas as medicine, decorative alloys and electronics have created the need for improved separational and determinative procedures. Of the many separational methods employed, solvent extraction processes are among the most popular. Consequently, a great variety of extraction methods have been proposed to isolate gold, often prior to its subsequent determination. However, few extractive methods have become available for the separation of gold when it is present with large amounts of the base metals or the platinum group metals.

Many of the solvent extraction procedures have been critically reviewed by Beamish [6].

Most of the early methods are based upon the extractability of the tetrabromo or tetrachloro-aurate complexes into various solvents such as ethers or esters.

The use of ethyl acetate as an extractant for gold has been utilized by several researchers to separate gold from copper [38], platinum [39], meteorites [40], rocks and various minerals [41].

The extraction of gold with methyl isobutyl ketone (MIBK) from hydrochloric acid solutions has been studied [42].

Strong and Smith [43] have analyzed sulfide ore and concentrate samples for gold by MIBK extraction and subsequent atomic absorption analysis.

Recently Diamantatos and Verbeeck [44] used MIBK to separate gold from the platinum metals.

Trioctylamine and trioctylmethylammonium chloride have been used to extract gold from ore samples [45] and synthetic solutions containing some of the base metals [46].

A quantitative separation of gold (III) by extraction with 4-methyl-2-pentanol in benzene from the platinum and some of the base metals has been described by Patil and Shinde [47].

Ziegler and Winkler [48] used tetrahydrofuran in methylene-chloride to extract gold from large amounts of some of the base and platinum metals.

Walker and Holland [29] have previously studied the extraction of milligram amounts of gold after reaction with 4-heptanone oxime into chloroform. The effects of hydrochloric acid concentration, oxime concentration and multiple extractions were described.

The purpose of the present work is to investigate the development of a quantitative procedure for the extraction of gold at the microgram level after reaction with 4-heptanone oxime into chloroform. The recovery of trace amounts of gold (III) from hydrochloric acid is studied. The separation of

microgram amounts of gold (III) from milligram quantities of the base metals by the developed recommended procedure is given.

B. Experimental

1. Apparatus and Materials

a) Instruments

Spectrophotometric measurements were made with a Beckman DB spectrophotometer 1.00 cm. matched cells. A Prazisions pH meter model E510 was used for pH measurements. All separatory funnels used were fitted with teflon stopcocks.

b) 4-heptanone Oxime

The 4-heptanone oxime was prepared by reaction of 4-heptanone with hydroxylamine hydrochloride as previously described [19] in Part II.

c) Gold Sponge

Spectrographically analyzed gold sponge greater than 99.99% pure was obtained from Johnson Matthey Chemical Ltd.

d) Standard Gold (III) Chloride Solution

A stock solution was prepared by dissolving an accurately weighed amount of spectral pure gold sponge in 25 ml. of aqua regia, evaporating repeatedly with hydrochloric acid and diluting to 1 litre with 1 M hydrochloric acid. An appropriate diluted standard solution was made from the above stock solution, to contain approximately 15 µg. per ml.

e) Base Metal Salts

The iron (III) chloride hexahydrate, nickel (II) chloride hexahydrate and copper (II) chloride dihydrate were A.C.S. grade.

f) Miscellaneous Reagents

All acids and bases used were of A.C.S. grade. The potassium chlorate, potassium perchlorate, sodium bicarbonate

and sodium fluoride were all A.C.S. grade. Distilled deionized water was used throughout.

g) Solvents

A.C.S. grade chloroform and A.C.S. spectral grade methylene chloride and methanol were used.

h) Standard Nickel (II) Chloride Solution

A stock solution was prepared by dissolving 81 grams of nickel (II) chloride hexahydrate in about 1 litre of distilled deionized water. Concentrated hydrochloric acid was added so that the solution would be 0.1 M in hydrochloric acid upon dilution to the 2-litre mark. The solution was standardized gravimetrically with dimethylglyoxime.

i) Standard Copper (II) Chloride Solution

A stock solution was prepared by dissolving 53.6 grams of cupric chloride dihydrate in about one litre of distilled deionized water; enough concentrated hydrochloric acid was added so that the solution would be 0.1 M in hydrochloric acid upon dilution to the 2-litre mark. An appropriate aliquot was withdrawn and standardized against a standard sodium thiosulfate solution iodometrically.

(j) Standard Iron (III) Chloride Solution

A stock solution was prepared by dissolving 64.5 grams of ferric chloride hexahydrate in 1 litre of distilled deionized water. Enough concentrated hydrochloric acid was added so that the solution would be 0.1 M in hydrochloric acid upon dilution to the 2-litre mark. An appropriate aliquot was withdrawn and standardized titrimetrically with potassium dichromate.

k) Chloric Acid [49]

Prepared by weighing 500 grams of potassium chlorate into a 3-litre beaker, adding 900 ml. of distilled water and heating on a hot plate until dissolved. The beaker was removed from the hot plate and 375 ml. of 72% perchloric acid was added with constant stirring. The covered beaker was kept in a refrigerator for 24 hours to effect complete precipitation of the potassium perchlorate. The solution was filtered on a buchner funnel with suction through a Whatman 541 filter paper. The filtrate contains approximately 28% chloric acid. The solution was stored in a refrigerator.

l) Buffer Solution

A buffer solution, pH 3.0, was prepared by mixing 50 ml. of 0.1 M potassium hydrogen phthalate and 22.3 ml. of 0.1 M hydrochloric acid.

m) Sodium Fluoride Solution

A sufficient quantity of sodium fluoride was dissolved in distilled water to give a final concentration of 10 mg./ml. of fluoride. The solution was stored in a polyethylene bottle.

2. Procedures

a) Studies to Determine a Recommended Procedure of Extraction for Microgram Amounts of Gold (III)

An initial investigation revealed that following the recommended triple extraction procedure outlined by Walker for the extraction of milligram amounts of gold (III) resulted in very low recoveries of gold (III) when taken at the microgram level. The results of this study are given in Table IV.

From this investigation, it became apparent that it would be necessary to alter Walker's procedure in order to develop a method of extracting gold (III) at the microgram level.

The effect of varying the reaction time, the total volume of 4-heptanone oxime used, and the number of extractions performed from solutions 0.1 M in hydrochloric acid were studied. The chloroform layers involved in these studies were analyzed for gold according to the procedure outlined below. The optimum conditions found in these studies then became part of the recommended procedure for the extraction of microgram quantities of gold (III). The results of these studies are summarized in Table V.

b) Recommended Procedure for the Extraction of Microgram Amounts of Gold (III)

Transfer a 7 ml. aliquot of the diluted standard gold (III) chloride solution containing 105 µg. of gold, to a 250 ml. graduated separatory funnel. Add 6 ml. of saturated potassium perchlorate and dilute to the 100 ml. mark with 0.1 M hydrochloric acid. Transfer 1.5 ml. of 4-heptanone oxime to the separatory funnel, and shake for 60 seconds. Extract with two 25 ml. portions of chloroform, shaking for 20 seconds during each extraction. Transfer the chloroform extracts to a 180 ml. electrolytic beaker containing a glass bead.

c) Gold Analysis of the Chloroform Extracts

Cover the 180 ml. electrolytic beaker with a speedy vap watch glass and evaporate the chloroform to dryness. To

the beaker add 10 ml. of chloric acid. Place the covered beaker on a hot plate and digest with evaporation to complete dryness in a perchloric acid fume hood. Heat the crystalline residue until dense white fumes of perchloric acid cease to evolve. To the cooled beaker add 3 ml. of aqua regia. Cover with a speedy vap watch glass, and evaporate to near dryness. At this point, add 4-5 drops of aqua regia and wash the watch glass and sides of the beaker with concentrated hydrochloric acid. It is important to note that the contents of the beaker should not be allowed to evaporate to dryness since gold is easily reduced and low recoveries will be obtained. Continue heating with 2 to 3 repeated additions of concentrated hydrochloric acid until the oxides of nitrogen are completely removed.

To the cooled beaker add 5 ml. of a buffer of pH 3.0, 3 ml. of a saturated potassium perchlorate solution and 1 ml. of a sodium fluoride solution. Adjust the solution to pH 3.0 by addition of sodium bicarbonate and transfer to a 100 ml. separatory funnel. The gold is then determined spectrophotometrically with 2,2'-dipyridyl ketoxime [14].

The results of the recovery of 105 µg. of gold (III) from 100 ml. of 0.1 M hydrochloric acid using the outlined procedure are given in Table VI.

d) Extraction of Gold (III) from Solutions Containing Milligram Quantities of Copper (II), Iron (III) and Nickel (II)

Aliquots of the standard copper (II), nickel (II) and iron (III) chloride solutions were transferred (separately) to a 250 ml. graduated separatory funnel containing 105 µg.

of gold (III) and 6 ml. of saturated potassium perchlorate. The solution was diluted to the 100 ml. mark with 0.1 M hydrochloric acid. The recommended extraction procedure outlined above was followed, and the chloroform extracts were collected and analyzed for gold as previously described. In the case of extraction from copper chloride solutions 1 ml. of 1% EDTA was added just prior to the addition of 2,2´-dipyridyl ketoxime.

The results of this study are presented in Table VII.

TABLE IV

Extraction of µg. amounts of gold (III) according to Walker's recommended procedure for mg. amounts

Gold taken, 105 µg; Hydrochloric Acid Concentration 0.1 M; Total Volume of Oxime 1.5 ml. (3 x 0.5 ml.)

Gold Found in Water Layer, µg.	% Gold Recovered.
32.1	30.6
39.8	38.0

TABLE V

Effect of Multiple Extractions and Total Volume of 4-Heptanone Oxime

Gold taken, 105 µg.; Hydrochloric acid concentration 0.1 M; 60 second extraction time

Run	Total Volume of Oxime, ml.	Gold found in Chloroform extract, µg	% Gold found in Chloroform extract, µg
1	0.25 (1 x 0.25)	78.0	74.3
	0.25 (1 x 0.25)	81.5	77.5
2	0.50 (1 x 0.50)	98.0	93.3
	(1 x 0.50)	98.8	94.0
3	1.00 (1 x 1.00)	101.0	96.2
	1.00 (1 x 1.00)	101.0	95.7
4	1.00 (2 x 0.50)	92.5	88.1
	1.00 (2 x 0.50)	83.0	79.0
5	1.50 (1 x 1.50)	104.0	99.1
	1.50 (1 x 1.50)	103.0	98.0
6	2.00 (1 x 2.00)	90.3	85.9

TABLE VI

Extraction of Gold (III) by the Recommended Procedure

Gold taken 105 µg.; Hydrochloric Acid Concentration 0.1 M; Total Volume of Solution 100 ml.

Gold (III) found µg	% Gold Recovered
102	96.6
102	96.9
104	99.1
101	96.2
103	97.6
103	98.1
104	99.1
105	99.5
102	96.6
Avg. 103	Avg. 97.6

Standard deviation µg. 2.6

TABLE VII

Separation of Trace Quantities of Gold (III) from Milligram Quantities of Base Metals

Gold taken 105 µg; Hydrochloric Acid Concentration 0.1 M; Total Volume of Solution 100 ml.

Metal Salt	Equivalent** Amount of Metal taken mg.	Au (III)* found µg	Standard Deviation µg
Copper (II) chloride dihydrate	253	101	4.3
Iron (III) chloride hexahydrate	338	102	3.8
Nickel (II) chloride hexahydrate	496	103	2.5

* Each result is the average of twelve determinations.

** Upper tolerable limits of base metal using outlined procedure.

C. Results and Discussion

The earlier study of the reaction between 4-heptanone oxime and gold (III) chloride by Walker demonstrated that the hydrochloric acid concentration in the range of 0.001 to 0.2 M was not critical to the extraction of milligram amounts of gold (III). However, higher hydrochloric acid concentrations greatly reduced the recovery of the gold taken.

Dunn [50] has shown that even low concentrations of hydrochloric acid hydrolyze 4-heptanone oxime to yield the ketone and hydoxylamine hydrochloride. Hydroxylamine hydrochloride acts as a reducing agent which can reduce gold (III) to gold (I) or the elemental state. Thus this may be a reason for the decreased efficiency of the extraction of gold (III) at higher acid concentrations.

A preliminary study of the extraction of microgram amounts of gold (III) by Walker's recommended procedure for milligram amounts of gold (III) resulted in low recoveries (shown in Table IV).

With the purpose of developing a procedure for the extraction of trace amounts of gold (III), investigations were undertaken into the effect of varying the volume of 4-heptanone oxime, the number of extractions performed, and the reaction time.

In order to minimize the hydrolysis of 4-heptanone oxime, a hydrochloric acid concentration of 0.1 M was chosen for these investigations. It was also deemed necessary to use the highest acid concentration that could still effect

quantitative recovery, since further investigations were to be made as to the efficiency of this extraction procedure to separate trace amounts of gold (III) from associated base metals. Low acid concentrations could result in separation difficulties due to the hydrolysis of the base metals as well as gold itself.

The results of a study dealing with the reaction time indicated that the reaction of 4-heptanone oxime with gold (III) was complete after 30 seconds of shaking. A variance in time from 30 to 60 seconds was found not to be critical; however, at 90 seconds there was a decrease in the recovery of gold taken. This reduction in recovered gold was probably due to the hydrolysis of the reagent. The sixty second shaking time was chosen to be a constant in further studies.

The results of varying the total volume of 4-heptanone oxime and the number of extractions performed are given in Table V. These results indicate that greater than 95% of the gold (III) taken is extracted when a total of 1.0 to 1.5 ml. of the oxime is used in a single extraction.

The optimum conditions determined by these studies were then used in the development of the recommended procedure for the separation of microgram quantities of gold (III).

In the early stages the results of these studies were inconclusive owing to the poor recovery of gold. Often in the analysis of both the chloroform and water layer for gold content, a mass balance of 100% was not found. The problem was eventually determined to be a result of the method employed for destroying the 4-heptanone oxime-gold (III)

complex. Initially aqua regia was used to destroy the residual organic matter after evaportation of the chloroform. During the removal of the oxides of nitrogen by additions of hydrochloric acid the gold salts are easily reduced [51]. To overcome this problem, digestion was carried out with chloric acid.

Another problem was encountered when sodium hydroxide was used to adjust the pH to 3.0. This method also resulted in low recoveries of gold (III). Apparently when sodium hydroxide is added, momentary regions of high pH exist. In turn this results in the formation of unstable gold hydroxide which decomposes to yield elemental gold. For this reason sodium bicarbonate was employed to adjust the pH.

A study of the percent recovery of a series of extractions according to the recommended extraction procedure for gold (III) is given in Table VI. The results of this investigation indicated that an average of 97.6% of gold (III) taken at the 105 µg. level is extracted and the procedure can quantitatively recover gold (III) from 0.1 M hydrochloric acid.

Since the occurrence of gold in ores is often associated with the base metals, a study was made on the efficiency of the recommended procedure to separate trace amounts of gold (III) from copper, nickel and iron. The results of this study are summarized in Table VIII. They show that microgram amounts of gold (III) can be separated quantitatively from milligram amounts of copper (II), nickel (II) or iron (III) in 0.1 M hydrochloric acid solutions.

This last study indicates that this procedure for the separation of trace amounts of gold (III) from milligram amounts of copper, nickel and iron could lead to a method for the determination of trace amounts of gold in gold ores.

This procedure may provide a variety of useful adaptations for the determination of gold in such products as ores, concentrates, and industrial plant wastes.

D. Summary and Conclusions

A procedure is outlined for the quantitative separation of trace amounts of gold from 0.1 M hydrochloric acid solutions by the chloroform extraction of the gold (III) 4-heptanone oxime complex. This procedure is also effective for the separation of microgram amounts of gold (III) from milligram amounts of copper (II), iron (III) and nickel (II) in hydrochloric acid solutions.

A condensed version of this work has been published [52].

PART V

A SOLVENT EXTRACTION STUDY OF SILVER (I) NITRATE WITH 4-HEPTANONE OXIME

PART V

A SOLVENT EXTRACTION STUDY OF SILVER (I) NITRATE WITH 4-HEPTANONE OXIME

A. Introduction

In previous sections (Part II and III) it was demonstrated that trace amounts of palladium (II) after reaction with 4-heptanone oxime could be quantitatively separated from a noble-metals-bearing sulfide concentrate and from large-volume synthetic solutions containing macro amounts of iron, nickel, copper or cobalt.

In Part IV a 4-heptanone oxime solvent extraction procedure was developed to separate microgram amounts of gold (III) from milligram amounts of nickel, copper or iron.

The present work involves an investigation into the extractability of silver into chloroform after reaction with 4-heptanone oxime. In addition, it will describe a solvent-extraction study of the effect of nitric acid concentration, nitrate ion concentration, oxime concentration and silver (I) concentration on the distribution of silver (I) between aqueous and chloroform-4-heptanone oxime phases. Two models are developed to explain the distribution of silver (I).

Very few solvent extraction procedures for silver are reported in the literature. Among the methods for the extraction of trace amounts of silver, procedures based on

the extraction of its complex with dithizone into chloroform or carbon tetrachloride are the most widely used.

The tendency of silver to form extractable complexes with other reagents has been reported.

Schweitzer and Bramlitt [53] have investigated the extraction of the silver 8-hydroxyquinoline complex into chloroform.

Silver has been shown to form a stable complex with diethyldithiocarbonate [54] which can be quantitatively extracted into carbon tetrachloride.

Handley and Dean [55] have reported a useful extraction procedure for silver from 6 M nitric acid, based on the use of tri-iso-octylthiophosphate or tri-n-butylthiophosphate dissolved in carbon tetrachloride.

Pyridine has been used to separate milligram amounts of silver from comparable amounts of lead [56].

Tri-n-butylammonium chloride forms an extractable complex with silver. This method has been used to separate silver from several metal ions [57].

Recently Trybulowa et al. [58] reported the use of triphenylphosphine to separate trace amounts of silver from copper ores prior to its determination by atomic absorption.

B. Experimental

1. Apparatus and Materials

a) Instruments

Spectrophotometric measurements were made with a Beckman DB spectrophotometer using 1.00 cm. matched silica cells. Chloroform water solutions were swirled on a Lab Line Orbit Incubator Shaker at a constant temperature of 25°C.

b) Silver Nitrate

Silver nitrate was A.C.S. grade and obtained from Thorn Smith Chemical Company.

c) Standard Silver (I) Nitrate Solution

A stock solution was prepared by dissolving 3.149 gm. of previously dried Thorn Smith A.C.S. grade silver nitrate in distilled deionized water containing 1 ml. of standardized nitric acid and diluting to 1 litre.

d) Chloroform

All chloroform A.C.S. grade used in this investigation was passed through a column of silica gel to remove any traces of preservative ethanol. The chloroform was subsequently saturated with distilled deionized water and stored in a glass bottle.

e) Water

Distilled deionized water which had been chloroform-saturated was used for dilutions throughout these studies.

f) Miscellaneous Reagents

Redistilled nitric acid obtained from G. Fredrick Smith Chemical Company was standardized with sodium hydroxide

and used for all nitric acid concentration adjustments throughout this study. All nitrate ion concentration adjustments were made with Baker Analyzed A.C.S. grade sodium nitrate.

The Carbon tetrachloride used was of A.C.S. spectral grade; the sulfuric acid was A.C.S. grade.

g) 4-Heptanone Oxime

The reagent was prepared by reaction of 4-heptanone with hydroxylamine hydrochloride as previously described in Part II.

2. Procedures

a) Preliminary Study of the Chloroform Extraction of the Silver (I) Nitrate 4-Heptanone Oxime Complex

A 10-ml. aliquot of the standard silver (I) nitrate solution containing approximately 20 mg. of silver (I) was transferred to a 250 ml. separatory funnel. A known volume of nitric acid was added so that on dilution to the 100 ml. mark the solution would be 0.5 M in nitric acid. To the separatory funnel was transferred 2.5 ml. of 4-heptanone oxime. The solution was shaken for 60 seconds and then extracted with two 25 ml. portions of chloroform (20 seconds shaking time each). The chloroform extracts were transferred to a 400 ml. beaker. The above procedure was repeated twice more with the residual water layer, and the chloroform extracts were combined.

b) Silver Analysis of the Water Layer

The aqueous layer was transferred to a 400 ml. beaker

and evaporated to a small volume. Five ml. of concentrated nitric acid, and 5 ml. of concentrated sulfuric acid were added to the beaker. The solution was then evaporated on a hot plate to dryness. The resulting white crystalline material was re-dissolved by the addition of nitric acid and water, and the silver content determined spectrophotometrically with dithizone [59]. The results of this study are summarized in Table VIII.

c) Initial Equilibrium Study

To a 250 ml. stoppered erlenmeyer flask, a 5 ml. aliquot of the standard silver (I) nitrate solution and 45 ml. of 0.1 M nitric acid were added. Four ml. of 4-heptanone oxime diluted to 50 ml. with chloroform (equivalent to 0.536 M in oxime) was then added to the flask.

Several of these oxime-chloroform aqueous solutions were swirled at a constant temperature of 25° C. for 30 and 60 minutes. From analysis of the silver in the chloroform-oxime phase and the water phase, it was found that maximum extraction was reached after 30 minutes. Thus all samples in further studies were swirled for one hour to ensure complete equilibrium of the silver between the oxime-chloroform layer and the aqueous phase.

d) Effect of Nitric Acid Concentration on the Distribution of Silver (I)

A 5 ml. aliquot of the standard silver (I) nitrate solution was transferred to a 250 ml. stoppered erlenmeyer flask. A known volume of standardized nitric acid was added, and the volume was increased to 50 ml. with distilled water.

To this solution was pipetted 50 ml. of chloroform containing 4 ml. of 4-heptanone oxime. The flask was then swirled for 1 hour at 25° C. After swirling the mixture was transferred to a 250 ml. separatory funnel, and the two layers were allowed to separate. The chloroform-oxime layer and aqueous layer were drawn off into separate 400 ml. beakers and a silver analysis was performed on each phase. Each sample was prepared and run in duplicate. The results of this study are summarized in Table IX and illustrated in figure 2.

e) Analysis of Silver in the Oxime-Chloroform Phase

The separated chloroform-oxime layer was evaporated to dryness on a steam bath. To the remaining residual organic residue was added 5 ml. of concentrated sulfuric acid. To the sulfuric acid solution dropwise concentrated nitric acid was added, and the resulting solution was digested on a hot-plate. After the organic material was destroyed, the contents of the beaker were evaporated to dryness. The white crystalline material in the beaker was re-dissolved by the addition of nitric acid and water. The silver content was then determined either titrimetrically with potassium thiocyanate or spectrophotometrically with dithzone.

f) Silver Analysis of the Aqueous Phase

The water layer was transferred to a 400 ml. beaker, and the volume was reduced on a hotplate to approximately 5 ml. After cooling, a 10 ml. portion of 1:1 nitric sulfuric acid was added to the beaker. After digestion the silver content was determined following the same procedures as above.

g) Effect of Sodium Nitrate Concentration on the Distribution of Silver (I)

All samples were prepared and extracted as in the previous section 2-d except that the aqueous phase contained known amounts of sodium nitrate instead of nitric acid. All samples were run in duplicate and analysis of silver in the chloroform-oxime and aqueous phases was performed as previously described. The results of this investigation are given in Table X and illustrated in figure 3.

h) Effect of Varying the Silver (I) Concentration on the Distribution Ratio of Silver (I) at 0.50 and 0.05 M Nitric Acid Concentrations

All samples were prepared and extracted as in the previous acid study (section 2-d) except that the acid concentration was held at 0.05 or 0.50 M nitric acid and the silver (I) content of the aqueous phase was varied over the range of 2-9 mg. The procedure was carried out in duplicate, and the analysis of silver in the aqueous and chloroform-oxime layers was performed as previously described.

Results of this study are summarized in Tables XI and XII and illustrated in figure 4.

i) Effect of Varying the 4-Heptanone Oxime Concentration on the Distribution Ratio of Silver (I)

All solutions were prepared and extracted as outlined previously in section 2-d except that the acid concentration was held at 0.05 or 0.50 M in nitric acid and the oxime concentration in the organic phase was varied from 0.134 to 0.671 M. The procedures were carried out in duplicate.

After the 1-hour swirling period, the aqueous and organic

phases were separated and the corresponding silver content was determined as previously described.

Results of this investigation are summarized in Tables VIII and XIV and illustrated in Figure 5.

j) A Study of the Theoretical Predicted Recovery of Silver (I) from 0.7 M Nitric Acid

All samples were prepared and extracted as follows: twenty-five ml. of 0.7 M nitric acid containing approximately 5.0 mg. of silver (I) was added to a 250 ml. erlenmeyer flask. To the flask was added 75 ml. of chloroform 0.536 M in 4-heptanone oxime. The flask was stoppered and swirled for 1 hour at 25° C. The entire contents of the flask were then transferred to a 250 ml. separatory funnel.

The two layers were allowed to separate and the chloroform-oxime phase was collected in a 400 ml. beaker. The aqueous phase was transferred back to the erlenmeyer flask by rinsing with another 75 ml. of the chloroform-oxime mixture. The flask was stoppered and swirled again for 1 hour at 25° C. The chloroform-oxime phase was then quantitatively separated, and the silver content of the residual aqueous phase was determined as previously described by the dithizone procedure.

The results of this study are presented in Table XV.

TABLE VIII

Extraction of Silver (I) by a Triple Extraction Procedure

Silver taken 19.99 mg./100 ml. Nitric Acid concentration 0.5 M.
Total volume of oxime 7.5 ml. (3 x 2.5 ml.)
Total volume of $CHCl_3$ 150 ml. (6 x 25 ml.)
Shaking time 1 minute

Run	mg. of Silver found in water layer	% Silver Extracted
1	0.230	98.9
2	0.065	99.7
3	0.188	99.1
4	0.368	98.2
5	0.130	99.4
6	0.224	98.9
7	0.078	99.6
8	0.232	98.8
9	0.049	99.8
	Average Recovery:	99.2%

TABLE IX

Effect of Nitric Acid Concentration on the Extraction of Silver Nitrate into Chloroform 4-Heptanone Oxime

Solutions: 50 ml. of $CHCl_3$ containing 4 ml. of 4-heptanone oxime

50 ml. of aqueous phase containing known amounts of HNO_3

Swirling time 1.0 hr. at 25° C

Silver taken 9.99 mg.

Molarity of HNO_3 in Aqueous Layer	% Ag(I) Extracted*	Distribution Ratio of Ag (I)
1.46×10^{-3}	20.6	0.259
4.46×10^{-3}	20.5	0.257
6.46×10^{-3}	24.6	0.326
1.15×10^{-2}	32.3	0.477
3.02×10^{-2}	52.3	1.10
5.02×10^{-2}	62.9	1.70
7.02×10^{-2}	68.4	2.17
9.02×10^{-2}	70.4	2.38
1.02×10^{-1}	72.2	2.60
3.02×10^{-1}	80.5	4.13
5.02×10^{-1}	84.8	5.58
7.02×10^{-1}	87.5	7.00
9.02×10^{-1}	89.0	8.05
1.10	90.7	9.75
1.30	89.2	8.26

*Average of duplicate analyses

EFFECT OF NITRIC ACID CONCENTRATION

ON THE DISTRIBUTION RATIO OF SILVER (I) NITRATE

Silver taken 9.99 mg.

Molarity of 4-heptanone oxime, 0.536

A - straight line portion up to 0.07 M

B - straight line portion from 0.1 M

FIGURE 2

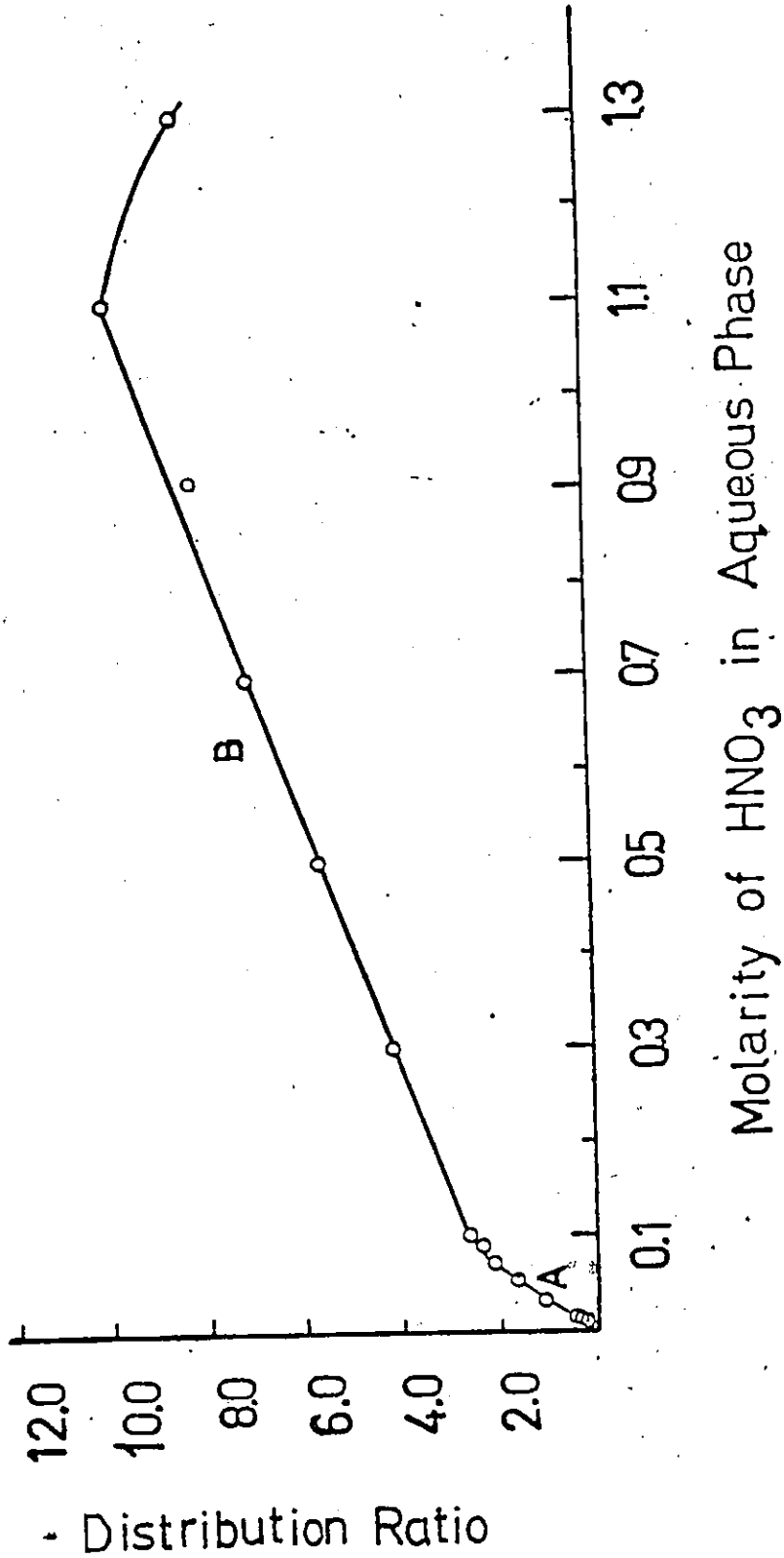

12.0
10.0
8.0
6.0
4.0
2.0
Distribution Ratio
A
B
0.1
0.3
0.5
0.7
0.9
1.1
1.3
Molarity of HNO_3 in Aqueous Phase

TABLE X

Effect of Nitrate Ion Concentration on the Extraction of Silver Nitrate into Chloroform 4-Heptanone Oxime

Solutions: 50 ml. $CHCl_3$ containing 4 ml. of 4-heptanone oxime

50 ml. aqueous phase containing known amounts of $NaNO_3$

Swirling time 1.0 hr. at 25° C

Silver taken 9.99 mg.

Molarity of NO_3 in Aqueous Layer	% Ag (I) Extracted*	Distribution Ratio of Ag (I)
4.29×10^{-3}	22.7	0.294
6.29×10^{-3}	23.9	0.314
8.29×10^{-3}	29.3	0.413
1.33×10^{-2}	33.5	0.504
3.33×10^{-2}	50.7	1.03
5.33×10^{-2}	62.1	1.64
7.33×10^{-2}	68.3	2.16
9.33×10^{-2}	70.6	2.40
1.03×10^{-1}	69.1	2.23
3.03×10^{-1}	82.5	4.71
5.03×10^{-1}	86.2	6.25
7.03×10^{-1}	88.8	7.92
9.03×10^{-1}	90.6	9.64
1.10	91.0	10.10
1.30	91.9	11.3

*Average of duplicate analyses

EFFECT OF SODIUM NITRATE CONCENTRATION

ON THE DISTRIBUTION RATIO OF SILVER (I) NITRATE

Silver taken 9.99 mg.

Molarity of 4-heptanone oxime 0.536

FIGURE 3

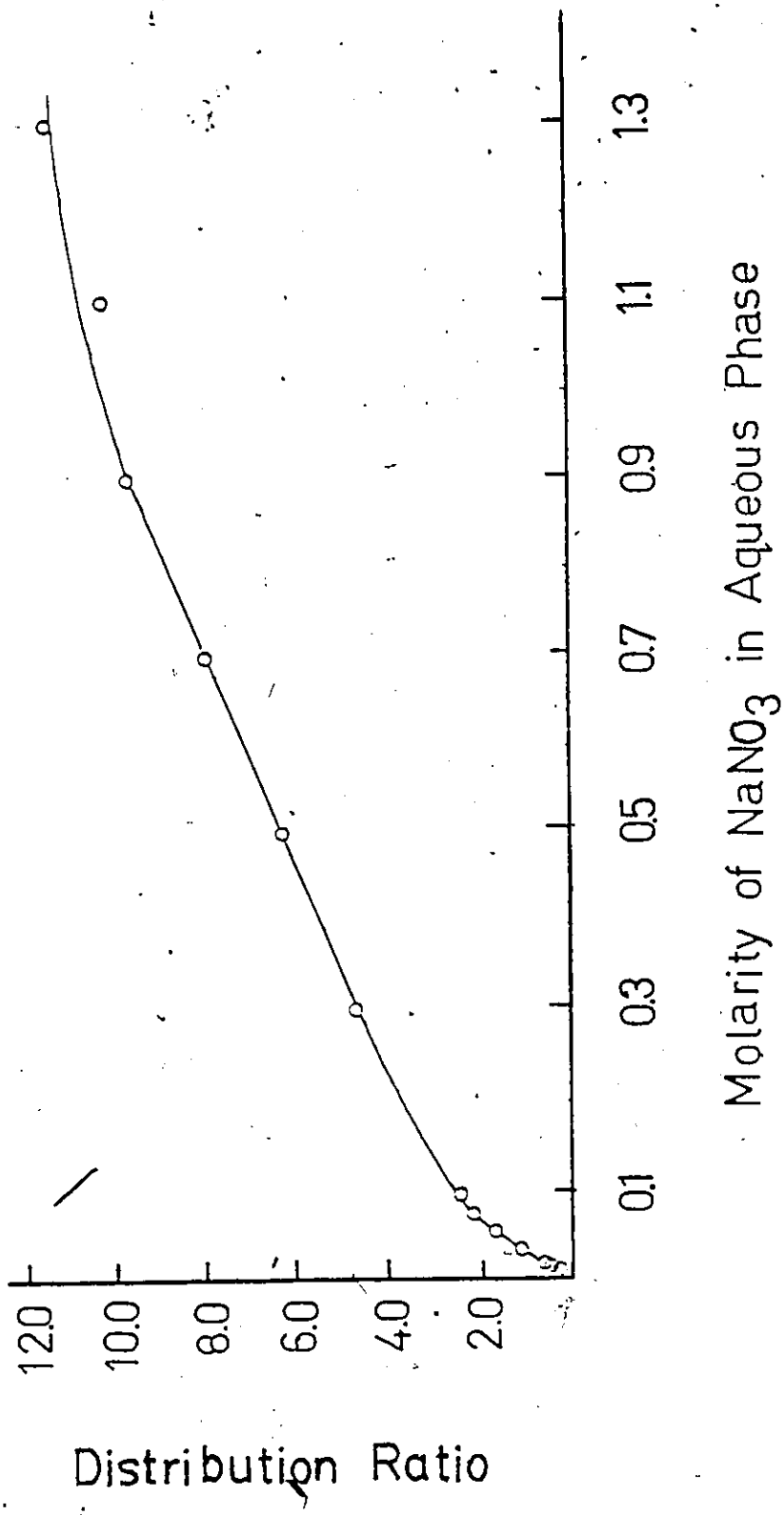

Distribution Ratio
12.0
10.0
8.0
6.0
4.0
2.0
0.1
0.3
0.5
0.7
0.9
1.1
1.3
Molarity of $NaNO_3$ in Aqueous Phase

TABLE XI

Effect of Varying the Silver Concentration on the Distribution Ratio of Silver (I)

Solutions: 50 ml. aqueous phase 0.05 M in HNO_3 containing known concentrations of Ag (I)

50 ml. 0.536 M 4-heptanone oxime in $CHCl_3$

Swirling time 1.0 hr. at 25° C

Molarity of Ag (I) in Aqueous Layer	% Ag (I) Extracted*	Distribution Ratio of Ag (I)
3.70×10^{-4}	64.4	1.81
7.41×10^{-4}	60.6	1.54
1.11×10^{-3}	60.6	1.54
1.48×10^{-3}	61.1	1.57
1.85×10^{-3}	62.9	1.70

*Average of duplicate analyses

TABLE XII

Effect of Varying the Silver Concentration on the Distribution Ratio of Silver (I)

Solutions: 50 ml. aqueous phase 0.50 M in HNO_3 50 ml.
0.536 M 4-heptanone oxime in $CHCl_3$
Swirling time 1.0 hr. at 25° C

Molarity of Ag (I) in Aqueous Layer	% Ag (I) Extracted*	Distribution Ratio of Ag (I)
3.70×10^{-4}	87.7	7.13
7.41×10^{-4}	87.4	6.94
1.11×10^{-3}	87.2	6.84
1.48×10^{-3}	86.7	6.54
1.85×10^{-3}	87.3	6.89

*Average of duplicate analyses

EFFECT OF VARYING SILVER (I) CONCENTRATION ON THE DISTRIBUTION RATIO OF SILVER (I)

-0- - Nitric acid concentration, 0.05

-□- - Nitric acid concentration, 0.50

Molarity of 4-heptanone oxime, 0.536

FIGURE 4

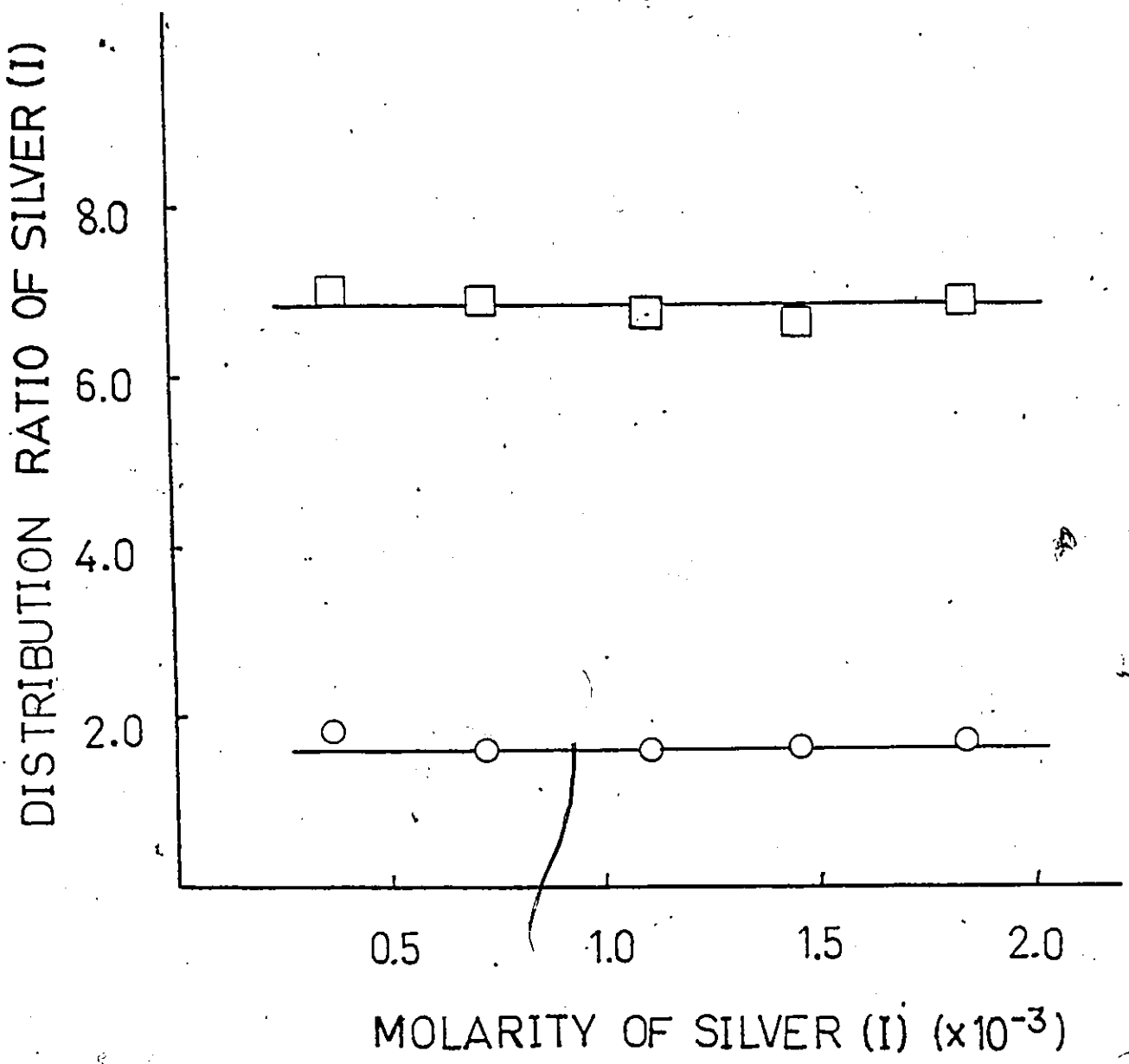

DISTRIBUTION RATIO OF SILVER (I)
8.0
6.0
4.0
2.0
0.5
1.0
1.5
2.0
MOLARITY OF SILVER (I) (x10⁻³)

TABLE XIII

Effect of Varying 4-Heptanone Oxime Concentration on the Distribution Ratio of Silver (I)

Solutions: 50 ml. of 0.05 M HNO_3 containing 9.98 mg. silver (I)

50 ml. $CHCl_3$ containing known concentrations of 4-heptanone oxime

Swirling time 1.0 hr. at 25° C

Molarity of 4-Heptanone Oxime in $CHCl_3$ Layer	% Ag (I) Extracted*	Distribution Ratio of Ag (I)
0.134	18.5	0.227
0.268	41.4	0.707
0.403	54.1	1.18
0.536	64.0	1.78
0.671	69.2	2.25

*Average of duplicate analyses

TABLE XIV

Effect of Varying 4-Heptanone Oxime Concentration on the Distribution Ratio of Silver (I)

Solutions: 50 ml. of 0.50 M HNO_3 containing 9.98 mg. of silver (I)

50 ml. $CHCl_3$ containing known concentrations of 4-heptanone oxime

Swirling time 1.0 hr. at 25° C

Molarity of 4-Heptanone Oxime in $CHCl_3$ Layer	% Ag (I) Extracted*	Distribution Ratio of Ag (I)
0.134	51.1	1.04
0.268	73.8	2.82
0.403	82.0	4.54
0.536	84.8	5.56
0.671	87.1	6.94

*Average of duplicate analyses

EFFECT OF VARYING *A*-HEPTANONE OXIME CONCENTRATION ON THE DISTRIBUTION RATIO OF SILVER (I)

C - -0- Nitric Acid Concentration, 0.05

D - -□- Nitric Acid Concentration, 0.50

Silver taken, 9.98 mg.

FIGURE 5

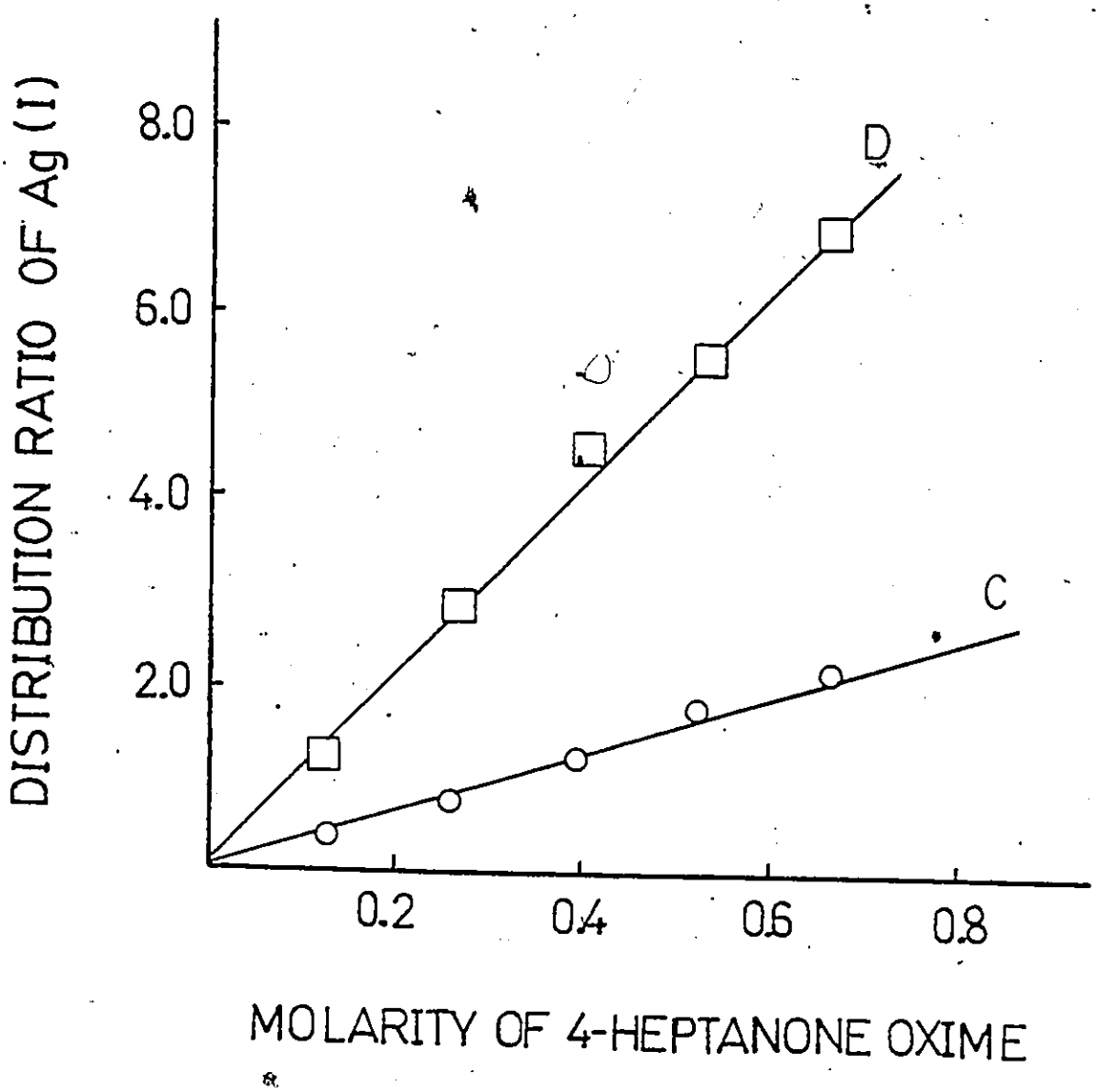

DISTRIBUTION RATIO OF Ag (I)
8.0
6.0
4.0
2.0
D
C
C
0.2
0.4
0.6
0.8
MOLARITY OF 4-HEPTANONE OXIME

TABLE XV

Extraction Study of Silver (I)
at 0.70 M Nitric Acid Concentration

Solutions: 2 x 75 ml. of $CHCl_3$ containing 6 ml. of 4-heptanone oxime (corresponding to 99.79% theoretical extraction)

25 ml. of 0.70 M HNO_3 containing 5.046 mg. of Ag (I)

Swirling time 2 x 1.0 hr. at 25°C

Run	Silver (I) Found in Aqueous Layer ug	% Silver (I) Extracted
1	5.13	99.90
2	13.00	99.74
3	0.55	99.99
4	1.20	99.82
5	0.43	99.99
6*	--	--

*No Silver (I) detected

Average of five results 99.89

C. Results and Discussion

A preliminary study of the reaction between silver (I) nitrate and 4-heptanone oxime indicated that relatively large amounts of silver (I) could be extracted into chloroform after reaction with 4-heptanone oxime in aqueous solutions 0.5 M in nitric acid. At the 20 mg. level, an average of 99.2% of the silver taken was recovered using a triple extraction procedure (Table VIII).

To better appreciate the course of the reaction between silver (I) and 4-heptanone oxime and the extraction process taking place, a solvent extraction study was initiated. Investigations of the effects of nitric acid concentration, nitrate ion concentration, oxime concentration and silver (I) concentration on the distribution of silver (I) between aqueous and 4-heptanone oxime-chloroform phases were undertaken. The resulting data can also serve in the development of a quantitative extraction procedure for silver (I).

The results of varying the nitric acid concentration are summarized in Table IX. A plot of this data (figure 2) seems to indicate that two courses of extraction are taking place: one in the straight line portion below 0.07 M nitric acid labeled A and the other in the straight line region above 0.1 M nitric acid labeled B. The significant drop in the distribution ratio at 1.3 M nitric acid is due to appreciable hydrolysis of the oxime at high acid concentrations.

Since it was noted that the nitric acid concentration appeared to effect changes in the course of the extraction of silver (I), it was decided to study the extraction

efficiency under different nitrate ion concentrations in order to see if the apparent change in silver extraction was due to acid concentration or nitrate ion concentration.

The effects of varying nitrate ion concentration are summarized in Table X and illustrated in figure 3. Again the data seems to demonstrate that two different extraction processes are taking place. In the region of low nitrate ion concentration a straight line is found from 0.01 to 0.07 M nitrate concentration. In the region from approximately 0.1 to 1.1 M nitrate another straight line of different slope is found.

The results of these two studies indicate that the nitrate ion concentration in the aqueous phase plays a direct role in the reaction course and subsequent extraction of silver (I). In order to explain these two different extraction processes and also to develop an equation to represent the distribution ratios at low and relatively high nitric acid concentrations, further studies were made at 0.05 M and 0.5 M nitric acid.

The results of a study dealing with the effect of varying silver (I) concentration, while holding the oxime concentration at 0.536 M and the nitric acid at 0.05 or 0.5 M in the aqueous phase are given in Tables XI and XII and illustrated in figure 4. The distribution ratios at both acid concentrations remained constant. Thus the results of this investigation demonstrated that the distribution ratio of silver (I) is independent of the silver (I) concentration in the aqueous phase at either low or high nitric acid concentration.

An investigation of the effect of varying 4-heptanone oxime concentrations in the chloroform phase with the aqueous phase at 0.05 and 0.5 M nitric acid are given in Tables XIII and XIV. A plot of this data (figure 5) shows two straight lines (C and D) of different slopes passing through the origin satisfying the general equation $y = m x$. These results indicate that the distribution ratios for silver (I) at low and relatively high nitric acid concentrations are directly proportional to the concentration of 4-heptanone oxime present in the chloroform phase.

The overall results of these studies demonstrate that the conditions of nitrate ion concentration in the aqueous phase and 4-heptanone oxime concentration in the organic phase are operable in the extraction of silver (I) into the chloroform-4-heptanone oxime phase.

To explain the results of these investigations, two models for the distribution ratios of silver (I) were developed.

Model I was used to explain the results of the extraction studies taking place from low nitric acid concentration while Model II explains the results found from relatively high nitric acid concentration. In the development of Model I a scheme for the extraction process taking place at low nitrate ion concentration and high 4-heptanone oxime concentration is shown as follows:

$$Ag^+ + Ox \rightleftharpoons AgOx^+ \qquad (1)$$

$$AgOx^+ + Ox \rightleftharpoons Ag(Ox)_2^+ \qquad (2)$$

$$Ag(Ox)_2^+ + NO_3^- \rightleftharpoons Ag(Ox)_2NO_3 \quad \text{(extracted)} \qquad (3)$$

Where Ox = 4-heptanone oxime

Thus model I for the distribution ratio of silver (I) can be expressed as:

$$D_1 = \frac{[Ag(Ox)_2NO_3]_o}{[Ag^+]_a + [AgOx^+]_a + [Ag(Ox)_2^+]_a} \quad (4)$$

where o = organic phase
a = aqueous phase

Several assumptions can be made with regards to this model. Since the concentration of 4-heptanone oxime is very high, the presence of Ag^+ in the aqueous phase can be considered negligible since it would react with oxime to form $AgOx^+$. The concentration of $Ag(Ox)_2^+$ in the aqueous phase can be assumed negligible since $Ag(Ox)_2^+ + NO_3^-$ forms $Ag(Ox)_2NO_3$, which is extracted. Also at low nitrate concentrations the formation of $AgOxNO_3$ is assumed to be negligible.

The distribution ratio of silver (I) can now be expressed as:

$$D_1 = \frac{[Ag(Ox)_2NO_3]_o}{[AgOx^+]_a} \quad (5)$$

This equation for the distribution ratio can be rewritten to show how it is directly proportional to the concentration of oxime in the organic phase and nitrate ion concentration in the aqueous phase. This is accomplished by considering the equilibrium processes taking place.

These equilibrium expressions can be described as

follows:

i) Reactions in Aqueous Phase

$$Ag^+ + Ox \overset{K_1}{\rightleftharpoons} AgOx^+ \quad (6)$$

$$AgOx^+ + Ox \overset{K_2}{\rightleftharpoons} Ag(Ox)_2^+ \quad (7)$$

$$Ag(Ox)_2^+ + NO_3^- \overset{K_3}{\rightleftharpoons} Ag(Ox)_2NO_3 \quad (8)$$

ii) Distribution of the Ion Association Complex

$$[Ag(Ox)_2NO_3]_a \overset{K_D}{\rightleftharpoons} [Ag(Ox)_2NO_3]_o \quad (9)$$

iii) Distribution of the Reagent

$$[Ox]_a \overset{K_{D'}}{\rightleftharpoons} [Ox]_o \quad (10)$$

In a previous study of the distribution of 4-heptanone oxime between water and chloroform, Dunn [60] reported that greater than 99% of the oxime is extracted into the chloroform phase. Thus for all practical purposes the concentration of 4-heptanone oxime in the chloroform is very nearly equal to its original concentration.

By suitable substitution of the previous equations (6-10) into eq. (5) the overall equation for the distribution ratio of silver (I) at low nitrate ion concentration becomes:

$$D_1 = \frac{K_D K_2 K_3}{K_{D'}} [Ox]_o [NO_3^-]_a \quad (11)$$

Let $K^* = \frac{K_D K_1 K_2}{K_D'}$

Then $D_1 = K^* [Ox]_o [NO_3^-]_a$ (12)

This equation now shows that the distribution ratios of silver (I) at low nitrate ion concentration are proportional to the oxime concentration in the organic phase times the concentration of nitrate ion in the aqueous phase.

The value of the distribution constant K* from eq. (12) can be determined from the results of the investigation of the effect of varying the nitric acid concentration in the aqueous phase while holding the oxime concentration constant (0.536 M) in the chloroform phase. A plot of these results (fig. 2) shows a straight line (A) passing through the origin of the type y = mx where the slope $m = k^* [Ox]_o$ from equation (12).

From the data in Table IX the average measured slope over the nitric acid range 0.01 to 0.07 is calculated to be 35.7.

Using the value of 35.7 for the slope of the line, the value of K* is determined by letting

$$K^* [Ox]_o = 35.7$$

$$K^* = \frac{35.7}{0.536} = 66.6.$$

From the study of the effect of varying the 4-heptanone oxime concentration while holding the nitric acid concentration constant at 0.05 M, a plot of the data (figure 5) gives

another straight line (C) passing through the origin of the general type $y = mx$.

The slope of line C from equation (12) would be $K^* [NO_3^-]_a$. Using the value found for K* and the concentration of nitric acid (0.05 M), the predicted slope of line C in figure 5 is 3.33.

The calculation of the slope of line C at a point where the concentration of 4-heptanone oxime is 0.536 M and the distribution ratio is 1.78 yields a value of 3.32; this agrees quite favourably with the predicted value of 3.33. Therefore, the K* value calculated from line A also holds for line C. Thus model I for the distribution ratio at low nitrate ion concentration and relatively high oxime concentration satisfies the experimental results.

In order to determine the composition of the silver complex a number of attempts were made to isolate the complexes from nitric acid layers before extraction or from chloroform layers after extraction. Variations in acid concentration and solvents, and evaporation under reduced pressure were unproductive. All attempts failed due to eventual decomposition with deposition of elemental silver.

Model II for the overall distribution ratio of silver (I) at relatively high nitrate ion concentrations and high concentrations of 4-heptanone oxime was developed from the following extraction scheme:

$$Ag^+ + Ox \rightleftharpoons AgOx^+ \qquad (13)$$

$$AgOx^+ + NO_3^- \rightleftharpoons AgOxNO_3 \quad \text{(extracted)} \qquad (14)$$

Model II for the distribution ratios of silver (I) is then expressed as:

$$D_2 = \frac{[AgOxNO_3]_o}{[Ag^+]_a + [AgOx^+]_a} \qquad (15)$$

Several assumptions can be made with respect to model II. In this case a ten-fold increase of nitrate ion is present over the previous model I. Therefore the concentration of $Ag(Ox)_2^+$ in the aqueous phase is assumed to be negligible since $Ag(Ox)_2^+$ either does not form, or if it does form, the high concentration of nitrate ion tends to displace an oxime molecule to form the extractable $AgOxNo_3$ complex.

The concentration of $AgOx^+$ in the aqueous layer can also be assumed to be negligible since at these high nitrate ion concentrations as soon as $AgOx^+$ forms it reacts with NO_3^- to form the extractable species $AgOxNO_3$.

Considering these assumptions, Model II for the distribution ratio of silver (I) at high nitrate ion and 4-heptanone oxime concentrations can be expressed as:

$$D_2 = \frac{[AgOxNO_3]_o}{[Ag^+]_a} \qquad (16)$$

This equation for the distribution ratio of silver (I) can be rewritten to show that it is directly proportional to the concentration of the 4-heptanone oxime in the organic phase and the nitrate ion concentration in the aqueous phase. This is done by considering the equilibrium processes taking place.

The reactions involved in the distribution of silver (I) nitrate between the oxime-chloroform phase and aqueous phase may be described as follows:

i) Formation of the Complex in Aqueous Phase

$$Ag^+ + Ox \overset{K_1}{\rightleftharpoons} AgOx^+ \quad (17)$$

$$AgOx^+ + NO_3^- \overset{K_2}{\rightleftharpoons} AgOxNO_3 \quad (18)$$

ii) Distribution of the Complex

$$[AgOxNO_3]_a \overset{K_D}{\rightleftharpoons} [AgOxNO_3]_o \quad (19)$$

iii) Distribution of the Reagent

$$[Ox]_a \overset{K_D}{\rightleftharpoons} [Ox]_o \quad (20)$$

By substitution of these equilibrium expressions, eq. (17-20) into eq. (16) the silver (I) distribution ratio, D_2 at high nitrate ion concentrations then becomes:

$$D_2 = \frac{K_D K_1 K_2}{K_D'} [Ox]_o [NO_3^-]_a \quad (21)$$

$$\text{let } K^{**} = \frac{K_D K_1 K_2}{K_D'}$$

$$\therefore D_2 = K^{**} [Ox]_o [NO_3^-]_a \quad (22)$$

This equation shows that the distribution ratio of the

silver (I) complex at high nitrate ion and oxime concentrations is a function of the concentration of the oxime in the organic phase and nitrate ion in the aqueous phase.

Equation (22) can be used to explain the results obtained from the previous investigations. In the study of the effect of varying the 4-heptanone oxime concentration while keeping the nitric acid concentration at 0.5 M, a plot of the results (figure 5) yielded a straight line (D) passing through the origin of the general type $y = mx$. From equation (22) the slope of this line m would be equal to $K^{**}\ [NO_3^-]_a$. Since the concentration of the nitric acid is held constant then $K^{**}\ [NO_3^-]_a$ is a constant K'.

Calculation of the slope of line D from Table XIV yields an average value of 10.1, which corresponds favourably to the experimentally measured slope of 10.6 found from figure 5.

A plot of the data from the investigation of the effect of varying the nitric acid concentration while the oxime concentration was held constant (Table IX, figure 2) resulted in a straight line (B) with a y intercept of 1.95. Line B satisfies the general equation of a line of the type $Y = mx + b$. From equation (22) the slope m would be equivalent to $K^{**}\ [Ox]_o$. Since the concentration of the oxime is held constant then $K^{**}\ [Ox]_o$ is a constant K''.

Equation (22) can be used to calculate the slope of curve B. Taking points from curves B and D where the oxime concentration is 0.536 M and the nitric acid is 0.50 M and substituting into equation (22) results in the following equations, for curve D:

$$5.56 = 0.536\ K' \qquad (23)$$

and for curve B

$$5.56 = 0.50\ K'' + 1.95 \qquad (24)$$

Since the slope of curve B was previously determined to be 10.6 then by substitution of this value into eq. (23), the slope of line B can be found. By equating eq. (23) to eq. (24) the slope of line B is calculated to be 7.46.

Measurement of the slope of curve B from the experimental results (Table IX) gives an average value of 7.23. Therefore the calculated value of 7.46 is in good agreement with the experimentally found value of 7.23. This indicates that model II for the distribution ratio of silver (I) at high nitrate ion concentrations and relatively high oxime concentrations satisfies the experimental results.

Again as in model I all attempts to isolate the silver oxime complex from nitric acid layers before extraction or from chloroform layers after extraction failed.

Considering equation (12) from model I ($D_1 = K^* [NO_3^-]_a [Ox]_o$) where the nitric acid concentration is held at 0.05 M and equation (22) from model II ($D_2 = K^* [NO_3^-]_a [Ox]_o$) where the nitric acid concentration is held at 0.50 M, a ratio of the two models would therefore yield a constant, i.e.

$$\frac{D_2}{D_1} = K^{***}.$$

From the results of the study dealing with the effects

TABLE XVI

Ratio of Distribution Ratios of Silver, (I)

D_2 Distribution ratio of silver at 0.5 HNO_3 and known oxime concentrations

D_1 Distribution ratio of silver at 0.05 HNO_3 and known oxime concentrations

Concentration of 4-heptanone oxime	D_2	D_1	D_2/D_1
0.10	1.05	0.31	3.39
0.20	2.09	0.62	3.37
0.30	3.10	0.93	3.33
0.40	4.15	1.25	3.32
0.50	5.15	1.55	3.32
0.60	6.20	1.87	3.31
Average			3.33

of varying the 4-heptanone oxime concentration and keeping the nitric acid concentration at the levels given above, the ratio of the corresponding distribution values was found to be a constant as shown in Table XVI.

A general term used in solvent extraction studies to denote extraction efficiency is the recovery factor. The equation for this may be expressed as

$$r_f = 1 - \left(\frac{1}{D \frac{V_o}{V_a} + 1} \right)^n \qquad (26)$$

where r_f = recovery factor

D = distribution ratio

V_o = volume of organic phase

V_a = volume of aqueous phase

n = number of extractions.

When a distribution ratio and parameters of an extraction procedure are known, equation (26) can be used to predict theoretically the recovery of a species. Alternately, if a distribution ratio is known eq. (26) can be employed in the development of a quantitative extraction procedure, or as a check to see if the distribution ratio is correct.

In the previous study of the effect of varying the nitric acid concentration on the distribution of silver (I), a number of distribution ratios were determined. It was decided to check one of these to see if it was correct and could be used in the development of a quantitative extraction procedure.

Using the distribution ratio of 7.000 found at 0.7 M nitric acid, a volume of 75 ml. of organic phase, 25 ml. of aqueous phase, and a double extraction, equation (26) theoretically predicts a recovery of 99.79% of the silver taken. The analysis of six samples (shown in Table XV) gave an average recovery of 99.89% which is in good agreement with the theoretically predicted value of 99.79%.

This study indicates that within experimental error, the distribution ratios found in earlier studies are correct and can be used in the development of extraction procedures to predict the recovery of silver (I).

D. Conclusions

The work in this study has demonstrated that silver (I) is extractable into chloroform after reaction with 4-heptanone oxime. The efficiency of the extraction procedure is dependent on two parameters, nitrate ion concentration and oxime concentration.

Results of the solvent extraction studies revealed that two different extraction processes take place, one from low nitrate ion concentration and the other from relatively high nitrate ion concentrations.

From the determination of the distribution ratios of silver (I), further investigations could be made into the development of truly quantitative (i.e. 99.9%) extraction procedures for trace and milligram amounts of silver. Also, methods for separating silver from associated base metals by 4-heptanone oxime extraction procedures are quite conceivable and should be investigated. From these studies procedures may then be developed which would be applicable to the separation and determination of silver in ores.

E. Summary

A preliminary study of the extraction of silver (I) nitrate after reaction with 4-heptanone oxime demonstrates that an average of 99.2% of silver (I) taken at the 20 mg. level is extracted. Solvent extraction studies are described as to the effect of nitric acid concentration, nitrate ion concentration, oxime concentration and silver (I) concentration on the distribution of silver (I). Two models are developed to explain the distribution of silver (I) from low nitric acid and high nitric acid concentration phases into chloroform-4-heptanone oxime phases.

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VITA AUCTORIS

1952 Born in Windsor, Ontario, January 19.

1966 Graduated from St. William's Grade School, Emeryville, Ontario.

1971 Graduated from Belle River District High School, Belle River, Ontario.

1974 Graduated from the University of Windsor, Windsor, Ontario, with the degree of Bachelor of Science in Geology.

1975 Accepted into Graduate School of the University of Windsor to study for the degree of Master of Science in Analytical Chemistry.

1977 Accepted into Graduate School of the University of Windsor to study for the degree of Doctor of Philosophy in Analytical Chemistry.

1978 Married to Rhonda Shannon Irwin of St. Clair Beach, Ontario, February 11.